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POLYNUCLEAR AROMATIC HYDROCARBONS (PAH)

BRUCE J. POITRAST, COLONEL, USAF, MC

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Final Report



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Aerospace Medical Division (AFSC)
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JOHN J. COUGHLIN, Colonel, USAF, B

Commander

Prepared by:

BRUCE J. POITRAST, Col, USAF, MC Consultant, Occupational Medicine

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I. INTRODUCTION

- A. Purpose: The purpose of this report is to discuss the hazard presented by polynuclear aromatic hydrocarbons (PAH) in soil and the workplace, to describe the requirements for soil treatment for these compounds, and to discuss potential occupational exposures which should be avoided.
- B. Problem: PAHs are compounds containing three or more fused benzene rings in any arrangement and containing no constituent other than carbon and hydrogen. They are ubiquitous and are formed by many combustion processes involving the burning of hydrocarbons. Scientists disagree about the relative contribution of various sources of PAH to the environment. Some would argue that the PAH in plants and soil are contaminants and not natural biological products (5, 17). Others believe that the majority come from natural sources such as forest fires, prairie fires, and volcanoes (11). Still others believe that the combustion of fossil fuels is the primary source (5, 6, 10, 14, 15, 17). These compounds may be found in foods either as the result of preparation, (charcoal broiling, smoking) or accumulation in the food chain (5, 6, 8).

Regardless of the source of the majority of these compounds, it is clear that power plants, automobiles, planes, and refuse burning are major sources. The soils and atmosphere surrounding highways, power plants, gas works, oil refineries and other industries contain levels of these compounds which are elevated compared to levels found in areas remote from these sources. PAHs are important to the Air Force because jet engines produce 40 grams per minute per engine during take off (6). Because of this the soil and air in the vicinity of runways may be heavily contaminated. Past methods of refuse disposal such as on-site burning and dumping of waste lubricating oil, have also contributed to the soil contamination problem.

C. Scope: This report will present basic information on the history of these compounds, their toxicity, work sites effected in the Air Force, and discuss some alternatives to disposal through removal to a land site.

II. DISCUSSION

A. Occupational Health Concerns of PAH in the Flying Community: In the flying community those who work directly with jet engines and their waste products are exposed to PAH. In the military, personnel who work in hardened aircraft shelters, engine noise suppression facilities or on the flightline can expect exposure to atmospheric PAH. Drag chutes deployed behind landing aircraft for braking purposes are heavily contaminated with hydrocarbons and in all likelihood with PAHs. Commonly, skin rashes of a photoactivated type are found in persons who work in these areas. Cracking, peeling and splitting of the skin are also relatively common due to the drying effect of hydrocarbons.



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- B. History: In 1775 Percival Pott, an English surgeon, first associated soot with cancer of the scrotum found in chimney sweeps in London. Nineteenth century coal tar workers and mule spinners had a high incidence of skin cancer. The mule spinners were prone to cancer of the scrotum because of daily contact with oil saturated clothing (7). In Japan in 1915, a pathologist, Yamagiwa, produced skin cancers in rabbits by frequent application of coal tar (6). The work of E.L. Kennaway, J. Hieger, W.V. Mayneord, J.W. Cook, and C.L. Hewett at the Institute of Cancer Research in Lohdon between 1922 and 1931 clearly established the chemical benzo(a)pyrene (BaP) as the responsible agent (11). Subsequent work has largely concentrated on the mechanism by which cancer is caused.
- C. Toxicity: Most PAHs are only weakly acutely toxic. They produce photoactivated dermatitis, eye and skin irritation. Chronic toxicity relates largely to carcinogenicity. Of 40 compounds listed by the National Academy of Sciences in 1972, 11 were strongly carcinogenic or mutagenic and 10 more were weakly carcinogenic or mutagenic (5).
- D. Metabolism: PAHs are absorbed by the skin, lung and intestine (17). When administered orally to animals, they are well absorbed and rapidly excreted in urine and into the bowel by way of bile. Relatively small amounts will remain in fat and the adrenals, and will persist for long periods of time (4, 6). PAHs are readily absorbed through the skin. Eighty percent of PAHs applied to the skin of mice was recovered in their feces over a seven day period (12). Once in the body, PAHs are metabolized by various routes. Microsomal oxidase forms epoxides which are hydrated by epoxide hydratase. Further micromosomal oxidase action forms other epoxides which are hydrated and excreted. A small fraction, as an epoxide, may combine with DNA (17).
- E. Movement in Soil, Water and Air: Movement in soil is a function of molecular weight and relative solubility in water and the organic content of the soil. Movement into lower soil layers from surface soils may not be appreciable but is highly variable (15). Surface water transport of free PAH is not a factor because of their susceptibility to photooxidation and rapid evaporation from water. Virtually 100% of free PAHs disappear from running water in less than 500 meters. They volatilize much less from standing water (14). Transport in water is largely by movement of PAH on particulate matter (16). The same is true for the movement of these substances in air. In air, 70-80% are moved on particulate. Unfortunately, most of these particles are largely in the 5μ range and are therefore of respirable size (10).
- F. Environmental Concentrations: The air above expressways has been sampled and found to contain as much as several hundred ng/m³ of PAH. Fly ash from incinerators may contain as much as 1000 ng/gram (10). Soil in a mixed forest in Massachusetts contained 1300 μ g/kg of BaP. It is generally accepted that the BaP represents no more than the 10% of the total PAHs found in soil. Thus it is likely that this soil contained 13,000 μ g/kg of total PAH at minimum (5). Soil from highways in Switzerland contained as much as 300,000 μ g/kg of soil of total PAH (5). The range was from 20,000 μ g/kg to 300,000 μ g/kg of PAH (2, 5).

- G. Perspective: Since PAHs have been found virtually everywhere that they have been sought and since some of the highest concentrations found anywhere are found by the roadside in every industrialized country in the world, it is not feasible, either physically or fiscally, to drum all this material and transport it to a hazardous waste storage site. Forms of on-site disposal must be considered. In the workplace, measurement of PAH in the atmosphere and on surfaces where they can be expected to be high seems a reasonable starting point.
- H. Factors for Consideration in On-Site Treatment of PAH: The parameters of interest to on-site treatment are as follows:
- 1. Rate of Degradation in Soil: Biological degradation of low molecular weight PAHs proceeds fairly rapidly. Higher weight PAH may require photooxidation first before biological breakdown can begin. If not exposed to air and sunlight, the half life of these compounds is increased by an order of magnitude. Others which cannot be directly metabolized can be metabolized in the presence of other carbon compounds (14). This has obvious implications for parameters two and three. The rate of degradation may be increased by low carbon fertilizers, bacterial innoculation, periodic aeration of soil and any other factor which can enhance bacterial, fungal or plant metabolism and the photooxidation processes. In the event that biological degradation is not a viable option, chemical methods, such as chlorine bleaches, may be considered. If the pH is kept above 6 this will result in oxygenated hydrocarbons rather than chlorinated ones.
- 2. Rate of Movement in Soil: This is largely determined by the ratio of solubility in soil to solubility in water. Solubility in soil is largely determined by the organic matter content of the soil. The rate of movement may be slowed by the addition of sorptive materials if necessary (charcoal, zeolite).
- 3. Proximity to Groundwater: This factor decides the acceptable limits for the other two. The product of rate of movement and rate of degradation must provide an acceptable margin of safety before the substances reach the water table.
- I. Determining Feasibility of and Methods for On-Site Treatment: Experimental methods must be used to determine both the feasibility of on-site treatment as well as the methods to be used. Column chromatography using soil from the site may be used to determine the rate of movement of contaminants in soil. Gas chromotographic mass spectrographic analyses may be used to define what kinds of toxicants are present in the soil. Biological assays will determine the ability of soil to destroy PAH. This will largely be related to the length of time the soil has been contaminated. The longer the period, the faster they will be degraded (14). The products resulting from treatment must be analyzed in the same fashion as the substances originally present. These too must degrade and move slowly in order that there is no spread of unacceptable substances. There must be some expectation that successful treatment will temporarily increase the site's toxicity. The use of oxidation processes will produce carcinogens in soil just the way it does in the body. This is acceptable as long as the contaminants do not spread and are ultimately reduced to harmless substances.

J. Approaches to Protection in the Workplace: PAHs are known to be high in the waste products of internal combustion engines. While at present no TLV exists for these substances, it would be reasonable not to expose workers on a regular basis to concentrations of these compounds which are greater than may be found in the atmosphere around highways. Contamination of work surfaces by these compounds should be readily handled by the washing of parts and surfaces before working on them, and, where that is not possible, using appropriate protective gloves.

III. CONCLUSIONS

Because PAH is found everywhere in the environment with some of the highest concentrations being found in soil near roads and highways, isolation of the population from PAHs is an impossible task. If we are to effectively remove PAH from the environment, methods for on-site treatment must be developed and used where possible. It is simply not physically or fiscally possible to dig up, drum, ship and store the soil from every airport and highway in America. Consideration must be given to alternative treatments without losing sight of the potential dangers presented by these substances. The occupational health considerations of these compounds have not been developed enough. Consideration should be given to some relatively simple protective measures when dealing with elevated concentrations of these substances in the workplace. Appropriate workplace measurements should be taken and appropriate engineering controls and personal protective equipment should be utilized.

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